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| (54) Title: ENHANCED FOOD VITAMIN ADDITION BY MICROBEAD DELIVERY  |  |   |   |
| (57) Abstract<br><br>Vitamins are added to food by first impregnating porous microbeads with vitamins, and adding the microbeads to the food.   |  |   |   |

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ENHANCED FOOD VITAMIN ADDITION  
BY MICROBEAD DELIVERY

BACKGROUND OF THE INVENTION

This invention relates to the addition of vitamins to food, and in particular, to the addition of vitamins to food by impregnating porous microbeads with vitamins and adding the microbeads to the food. Vitamins are essential in the diet of animals and humans. One problem in ensuring that foods have an adequate shelf life is the stability of vitamins added to foods to fortify them, i.e., make them more nutritious so that the consumer receives an adequate vitamin intake. Oxidation is one of the prime aspects of the problem. Some vitamins (e.g., carotene) are easily oxidized on contact with air. Other vitamins are more slowly oxidized but can still oxidize during the shelf-life of the product.

The stability of vitamins to oxidation is a particular problem in certain types of food. There is considerable surface area for oxidation in many foods. For instance, in breakfast cereals, particularly flakes, air readily circulates and permeates the food particularly during manufacturing and after the product is opened by the consumer. There is considerable surface area for oxidation in many foods.

SUMMARY OF THE INVENTION

According to the current invention, a food product is dispersed in water-insoluble, porous

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Polymeric beads that have microporous passages in them impregnated with one or more vitamins. In narrower aspects of this invention, the beads can be coated with water-soluble coatings to entrap the vitamins in the beads until the beads are exposed to water. Alternatively, the beads can be coated with coatings that melt when heated so that the vitamins are not released until the food is heated. In addition, the entrapment of fat-soluble vitamins (e.g., vitamins A, D, E, and K) is believed to be enhanced because the porous polymeric beads of the present invention exhibit an affinity toward water-insoluble compounds such as fat-soluble vitamin K.

DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS OF THE INVENTION

In the present invention, a food product (or matrix) contains porous polymeric beads that have microporous passages impregnated with one or more vitamins. The vitamins include, but are not limited to, vitamins A, B, C, D, E and/or K. Also the term "vitamins" as used herein includes provitamins, and pharmaceutically acceptable salts of any of the aforesaid vitamins or provitamins. By "pharmaceutically acceptable salts" is meant non-toxic acid addition salts and alkaline earth metal salts of such vitamins. The salts can be prepared in in situ during the final isolation and purification of the vitamins, or separately by reacting the free-base or acid functions of such vitamins with a suitable organic acid or base. Representative acid addition salts include hydrochloride, hydrobromide, sulphate, bisulphate, acetate, oxalate, valerate, oleate, palmitate, stearate, laurate, borate, benzoate, lactate, phosphate, tosylate, mesylate, citrate, maleate, fumarate, succinate, tartrate, glucoheptonate, lauryl sulfate salts and the like. Representative alkali or

alkaline earth metal salts include sodium, calcium, potassium, and magnesium salts and the like.

By "food product" or "food matrix" is meant an edible substance that delivers nutrition or taste pleasure to humans or other animals. Food matrices include but are not limited to meats, baked goods (i.e. breads, cakes, cookies, and pies and the like), puddings, syrups, gums, and the like. Food matrices also include dry or condensed mixes that upon addition of water or other ingredients form an edible substance that can be eaten immediately or eaten after cooking or further processing. Mixes include baked good mixes, soup mixes, pudding mixes, and the like.

Food matrices also include liquid beverages and concentrates for liquid beverages. With liquid beverages or concentrates, the porous polymeric beads containing vitamins can be added to the liquid immediately before the product is packaged so the vitamin will not be lost. The vitamin is released to the drink from the beads during storage and shipment of the product. This release can be delayed by using a water-soluble coating that dissolves over time.

Food matrices also include powdered or granular mixes for liquid beverages that are mixed with water to produce liquid beverages. A powdered or granular beverage mix usually includes a beverage base that ordinarily has flavoring (e.g. coffee or citrus flavor) and often a sweetener and the like. Beverage bases are known in the art and include instant coffee, milk shakes, fruit drinks, and the like. The vitamin-impregnated microbeads of this invention can be coated with a water-soluble coating that dissolves to release vitamin upon addition of water to the mix. Alternatively, the beads can be coated with a coating (e.g.,

fat) that melts when hot water is added, a feature desirable in hot drink mixes such as cocoa or coffee.

The present invention contemplates the addition to the food matrix described above of water-insoluble porous polymeric beads preferably of a size not discernible to the consumer where the beads have porous passages impregnated with one or more vitamins described above. The preferred size range is between 10 and 100 microns, and the most preferred is between 20 and 50 microns. Preferably, the porous polymeric beads are coated with a coating that influences the release of the vitamins within the microporous passages in the porous polymeric beads. Such coatings include zein, wax, gum arabic, fatty acids, fats, food grade shellac, carbohydrates, silica, water-insoluble polymers (e.g., polyvinyl acetate), proteins such as casein, starches, dextrins, or modified or unmodified cellulosics such as ethyl, methyl, hydroxypropyl, or hydroxyethyl cellulose. The use of such coated beads controls the release of vitamins in the porous polymeric beads typically such that the vitamins within the beads are released at a time when the food product is used by the consumer.

The polymeric beads of this invention are polymerized in a fashion that the microporous passages are formed during polymerization. Such a procedure is described below. Residual monomers are then extracted as described below so that the beads can be impregnated with vitamins. The beads are then optionally coated with one or more coatings and added to the food matrix. The details of the microparticle polymerization, monomer extraction, and microparticle impregnation and coating are described below followed by Examples I through V that illustrate various specific foods and polymeric beads of the present invention.

### I. POLYMERIC BEAD POLYMERIZATION

In one embodiment of the present invention, the polymeric beads can be polymerized as taught in U.S. Patent 4,690,825 to Won dated September 1, 1987, the entire disclosure of which is incorporated herein by reference. Specifically, the beads used in the food matrix of the present invention can be prepared by polymerizing one or more polymers by a free radical suspension polymerization process. A monomer or pair of comonomers is dissolved in an inert porogen to form a solution that is suspended in a phase or solvent incompatible with that solution. Such a phase or solvent can be water with stabilizing additives. After the solution is suspended in the phase, the solution and phase are agitated to form droplets of solution suspended in the phase. After the formation of the droplets, the monomer or monomers in the droplets are activated to initiate a polymerization reaction in which the monomer is cross-linked or where two or more monomers are polymerized to form porous beads having a network of pores with the porogen within the network of pores. The activation may be triggered by an initiator that is insoluble with the monomer solution. Alternatively, activation may be triggered by an energy source such as radiation. The inert porogen serves as an internal diluent during polymerization and introduces the desired sponge-like microporous structure or network of pores into the finished bead. The inert porogen does not react with the monomer present during polymerization or inhibit the polymerization. The beads may or may not swell in the inert porogen. After formulation of the porous beads, the beads are separated from the phase and subjected to one or more extraction steps such as washing to remove any unreacted monomer or impurity from the beads. After extraction, described below, the beads may be dried to obtain a powder-like

substance that includes the beads but without either porogen or solvent.

An example of a polymer that can be used to form porous polymeric beads for the food product of this invention is a copolymer of divinylbenzene and styrene. Such beads can be polymerized in water as taught in the aforesaid Won patent or as described in Example I below. If such a copolymer is used, the monomers (which are not food approved additions) are typically not completely reacted, and excess monomer concentration should be reduced to levels less than 30ppm [as illustrated by the styrene monomer standards for food-grade styrene-butadiene rubber (Food Chemical Codex, 3rd Edition, pg. 42.)] if the beads are to be used in a food product. Typically, the amount of free cross linking agent (divinylbenzene) in the beads after polymerization is quite low compared with styrene because divinylbenzene has two reaction sites, and thus is more reactive than styrene. Thus, the extraction is primarily to extract styrene monomer, the divinylbenzene monomer present in the polymer already being close to or lower than the 30ppm value. An extraction procedure is explained in Section II below and in Example I.

To avoid or reduce the effort required in monomer extraction, one can copolymerize divinylbenzene with a food-grade monomer that can polymerize with divinylbenzene. By a food-grade monomer is meant any monomer that is a food additive permitted for direct addition to food for human consumption under 21 CFR, part 172 or substances generally recognized as safe under 21 CFR, part 182. Examples of such monomers are one or more of the following: estragole, limonene, carvone, eugenol and ocimene. Limonene is illustrative inasmuch as it is a naturally-occurring compound in

many citrus fruits. Still other examples are provided in Example IV, infra.

The food-grade monomer need not be extracted unless one wants to extract it for flavor reasons. But in many instances, the food-grade monomer may enhance the flavor of the food. Thus, any extraction of monomer after polymerization may only have to focus on divinylbenzene reduction, a comparatively simple proposition because it is already in comparatively low concentration.

## II. MONOMER EXTRACTION

If monomer extraction is desired or required, it can be accomplished by washing the beads first with water followed by several (preferably three) washings of isopropanol, four to five washings with acetone and four to five washings with hexane. The excess solvent is removed by evaporation under a nitrogen blanket to leave dry beads having a powder-like consistency.

## III. POLYMERIC BEAD IMPREGNATION WITH VITAMINS

The impregnation of pores in the polymeric beads with vitamins can be accomplished by soaking the beads in equal or greater weight of a solution containing the vitamin(s) of interest so that the beads are completely immersed in the solution. The impregnation proceeds over a period of at least six and preferably forty-eight hours. The impregnation may be carried out at a reduced temperature if the stability or volatility of the particular vitamin is of a particular concern. Of the total dry weight of the loaded beads after impregnation, 60% or even more may be vitamin. Such loadings are possibly using this procedure, although some bead/vitamin combinations will yield lower loadings.

When impregnating the microbeads with a water-soluble vitamin (e.g., B complex or vitamin C),

the vitamin should be dissolved in an aqueous solution to which the microbeads are added. When impregnating the beads with a fat-soluble vitamin (e.g., vitamins A, D or K), the vitamin should be dissolved in an oil or fat to which the microbeads are added. The fat or oil can be heated slightly if the stability of the vitamin permits so that the fat or oil can be absorbed readily into the microbeads. Alternatively, the fat or oil can be dissolved in an organic solvent so that the resulting solution is less viscous and can be absorbed more readily into the beads.

#### IV. POLYMERIC BEAD COATING

As indicated above, the porous polymeric beads are preferably coated with a coating that retards the release of the vitamins from the pores of the beads or prevents the premature release of the vitamins during storage. Illustrative coatings include water-soluble or permeable compositions such as hydroxypropyl methyl cellulose, sugars and the like. Depending on the thickness and porosity of the water-soluble or permeable coatings, such coatings retard the release of the vitamins in the pores of the polymeric beads by first requiring the coating to dissolve before the vitamin is released.

Water-insoluble coatings may also be employed. Such coatings include food grade shellac as disclosed in U.S. Patent No. 4,673,577 to Patel dated June 16, 1987 that is incorporated herein by reference. Water insoluble wax coatings also include waxes such as those disclosed in U.S. Patent Application Serial No. 07/137,114 entitled Method of Making Chewing Gum with Wax-Coated Delayed Release Ingredients by Steven E. Zibell that is incorporated herein by reference, and zein.

Fatty acids can also be employed as coatings for the beads. Fatty acids, depending on chain length, have varying water solubilities. A mixture of fatty acids can be prepared that has the desired degree of water solubility that controls the dissolution of the coating until the desired time. Combinations or mixtures of water-soluble and water-insoluble coating agents may be employed as coatings for the porous beads to control or release of the vitamins from the beads.

A variety of methods to coat the beads can be used. Several are described generally below, and in detail in the examples infra.

A. Spray Drying

An emulsion/solution of vitamin-impregnated beads and encapsulant is atomized into an air stream that evaporates the solvent to leave coated beads. A Niro spray dryer may be used. This technique should be used where the particular vitamin is exposed to air only for a brief period, if at all. It is believed to be a workable technique in some cases because when vitamins entrapped in the passages in the beads, they cannot be exposed to air very readily.

B. Spray Chilling

A suspension of beads in molten encapsulant is atomized and chilled to produce beads coated with encapsulant. This technique can be used for vitamins such as niacin which are quite stable to heat. However, it should be used cautiously where the temperature of the melted encapsulant is higher than a temperature where a particular vitamin may degrade. Such temperatures are known to one of ordinary skill in the art, so the selection of an appropriate encapsulant is believed to be within the ability of one of ordinary skill in the art.

C. Fluid Bed Coating

Beads are suspended in an air stream (fluidized bed). The beads are sprayed with a solution of the encapsulant in a volatile solvent. The solvent is evaporated or dried by the air stream to produce beads coated by the encapsulant. The technique can be used where no short-term oxidation problems are experienced with a particular vitamin.

D. Granulation/Agglomeration

A damp mix of beads and granulant is prepared, then dried and ground to desired particle size. This is a preferred mode of coating beads for encapsulating vitamins except those that may be moisture sensitive when exposed to air (e.g., ascorbic acid). In such cases, it may be desired to prepare the mix in an oxygen-free environment (e.g., under a nitrogen blanket).

E. Gel Encapsulation

Beads are suspended in a gelatin solution that is cooled to gel, then ground to desired particle size.

F. Melt Blending

Beads are mixed into a molten agglomerant which is cooled to harden and ground to the desired particle size. Again, the choice of agglomerant should be made to have a melting temperature below the temperature where the particular vitamin may be unstable.

V. ADDITION OF BEADS TO THE FOOD PRODUCT

The vitamin-impregnated microbeads of this invention can be added to a food matrix in a variety of ways. The food can be wet, and the beads added by mixing them into the food mechanically. The food can then be dried, preferably at a temperature lower than a temperature where vitamin stability is compromised.

Exposing the product to reduced pressures during drying helps to keep the temperatures sufficiently low. A good example of such formulation techniques is a breakfast cereal. The vitamin-impregnated beads are mixed in the cereal while the cereal is wet, and the cereal is dried under reduced pressure at a temperature less than 100°C to form a dried cereal. The dried cereal may be of the type to be cooked later, or consumed without cooking.

Other methods of adding vitamin-impregnated microbeads to foods include dry blending the microbeads in a dry food mix (e.g. a bread or cookie mix) before hydration and baking; or formulating the beads into a slurry that is sprayed onto the food.

The following examples of the invention are provided by way of explanation and illustration. They are not intended to limit the invention.

#### Example I

##### Thiamine - Fortified Cookie Dough

###### A) Preparation of Microbeads

Gelatin (250 mg) is added to a three-necked flask purged with nitrogen. Water (150 ml) is heated to 50°C and added to the flask to dissolve the gelatin. While the contents of the flask are stirred, a freshly prepared solution of benzoyl peroxide (1.25 grams; 1.03 mmole) and styrene (22.9 grams; 0.22 mole) monomer is added, followed by divinylbenzene (12.0 grams; 42 mmoles). The mixture is heated to 90°C while maintaining a constant stirring rate, and passing nitrogen through the flask.

The mixture is stirred for two hours, and cooled to room temperature, and the supernatant liquid is decanted. The polymer beads are washed with hexane several times, and stirred in hexane (200 ml) for two hours to remove any excess divinylbenzene or styrene,

and dried overnight at 50°C in a vacuum to yield dry microbeads.

B) Impregnation of Beads with Thiamine Chloride Hydrochloride

The beads prepared in part A are soaked in an equal weight of a 50% aqueous solution of thiamine chloride hydrochloride for 48 hours. The beads are filtered from solution. The beads are cooled to -20°C in a vacuum to remove the water.

C) Thiamine - Fortified Cookie Dough

The beads of part B are mixed with the ingredients in Table I to produce a dry cookie dough.

Table I

| <u>Ingredient</u>  | <u>Amount (grams)</u> |
|--------------------|-----------------------|
| Flour              | 100.0                 |
| Salt               | 0.93                  |
| Shortening         | 28.4                  |
| Sucrose            | 57.8                  |
| Sodium Bicarbonate | 1.1                   |
| Dextrose           | 0.9                   |
| Microbeads         | 0.14                  |

The cookie dough of Table I is mixed with a sufficient amount of water so that the dough is thick and tacky to the touch. The cookies are baked at 350°F until brown.

Example II

Bread Dough Fortified With Vitamin A

A) Vitamin A - Impregnated Beads

The microbeads prepared in Example I part A are immersed in an equal weight of a solution containing one part vitamin A and nine parts vegetable oil. The microbead mixture is stored for 48 hours at

room temperature in a dark room. The excess solution is filtered from the beads.

B) Vitamin A. - Fortified Bread Dough

The microbeads of part A are added to the ingredients in Table II to produce a dry bread dough.

Table II

| <u>Ingredient</u> | <u>Amount (grams)</u> |
|-------------------|-----------------------|
| Flour             | 40.0                  |
| Yeast             | 2.0                   |
| Sucrose           | 0.5                   |
| Beads             | 0.016                 |

The dry bread dough is made into a bread by adding a sufficient amount of warm water to the dry mix above to make a pliable, tack-free dough. The dough is allowed to rise, kneaded, and allowed to rise a second time. It is then placed in a bread pan, and baked at 350°F until golden brown.

Example III

Vitamin - Fortified Breakfast Cereal Flakes

A) Microbeads Impregnated With Thiamine, Riboflavin and Niacin

Microbeads prepared as described in Example I part A are immersed in a aqueous solution containing equal amounts of thiamine, riboflavin, and niacin. The excess solution is removed by filtration.

B) Vitamin - Fortified Breakfast Flakes

The beads of part A are formulated into a slurry of water (24%), sucrose (75%) and beads (1% by weight). The sugar slurry is sprayed onto conventional breakfast cereal flakes (e.g. corn or bran flakes). The water is evaporated during spraying to produce

breakfast flakes fortified with thiamine, riboflavin and niacin.

Example IV

Alternative Microbead Formulations

Various microbead polymers are possible consistent with the teachings of this invention. A number of types of microbeads can be prepared following the procedure set forth in Example I part A, altering the amount of monomer to be polymerized with divinylbenzene, or changing the monomer to be polymerized with divinylbenzene. Alternatively, the amount of divinylbenzene can be varied. A summary of such microbead formulations is set forth in Table III below.

Table III

|    | <u>Monomer</u>               | <u>Monomer Amount</u> | <u>Divinylbenzene Amount</u> |
|----|------------------------------|-----------------------|------------------------------|
| a) | Estragole                    | 32.6 g; 0.22 mole     | 33 g                         |
| b) | Estragole                    | 32.6 g; 0.22 mole     | 98 g                         |
| c) | Allyl cyclo-hexyl propionate | 43.12 g; 0.22 mole    | 12 g                         |
| d) | Allyl cyclo-hexyl propionate | 43.12 g; 0.22 mole    | 33 g                         |
| e) | Allyl cyclo-hexyl propionate | 43.12 g; 0.22 mole    | 97 g                         |
| f) | Ocimene                      | 29.92 g; 0.22 mole    | 12 g                         |
| g) | Ocimene                      | 29.92 g; 0.22 mole    | 33 g                         |
| h) | Ocimene                      | 29.92 g; 0.22 mole    | 97 g                         |
| i) | Divinyl-sulfide              | 18.96 g; 0.22 mole    | 12-97 g                      |

|    | <u>Monomer</u>            | <u>Monomer Amount</u> | <u>Divinylbenzene Amount</u> |
|----|---------------------------|-----------------------|------------------------------|
| j) | Vinyl methylketone        | 15.42 g; 0.22 mole    | 12-97 g                      |
| k) | 4-methyl-5-vinyl thiazole | 27.5 g; 0.22 mole     | 12-97 g                      |
| l) | 2-methyl-5-vinyl pyrazine | 26.1 g; 0.22 mole     | 12-97 g                      |
| m) | Vinyl pyrazine            | 23.32 g; 0.22 mole    | 12-97 g                      |
| n) | 1-penten-3-ol             | 18.92 g; 0.22 mole    | 12-97 g                      |
| o) | 1-octen-3-ol              | 28.16 g; 0.22 mole    | 12-97 g                      |
| p) | carvone                   | 33.00 g; 0.22 mole    | 12-97 g                      |
| q) | limonene                  | 29.92 g; 0.22 mole    | 12-97 g                      |
| r) | diallyl-disulfide         | 32.18 g; 0.22 mole    | 12-97 g                      |
| s) | allylsulfide              | 25.13 g; 0.22 mole    | 12-97 g                      |
| t) | allyl al-pha ionone       | 51.12 g; 0.22 mole    | 12-97 g                      |

The monomers identified above to be polymerized with divinylbenzene can also be combined with styrene to yield the desired beads. In addition, divinylbenzene can be replaced with allylacrylate as the crosslinker or with other suitable divinyl compounds.

Microbeads produced from the polymers described above are made from food-grade monomers that can polymerize with divinylbenzene. The residual food-grade monomer in the microbeads can contribute flavor to the food. Accordingly, to achieve a proper blend of food-grade monomer with the flavoring of the food to achieve good taste, certain combinations of food-grade monomer and food flavorings are preferred, as indicated in Table VI below.

Table VI

| <u>Food Flavoring</u> | <u>Monomer(s)</u>   |
|-----------------------|---|
| Mint                  | Estragole, ocimene, vinyl-methyl ketone, 1-octen-3-ol, 1-penten-3-ol, carvone, limonene, allyl alpha ionone |
| Onion                 | Divinylsulfide, diallyldisulfide, allylsulfide  |
| Citrus                | Ocimene, carvone, limonene  |
| Peanut                | 4-methyl-5-vinylthiazole, 2-methyl-5-vinylpyrazine, vinylpyrazine   |
| Meat                  | 4-methyl-5-vinylthiazole, 2-methyl-5-vinylpyrazine, vinylpyrazine, diallyldisulfide, allylsulfide           |
| Fruit                 | Eugenol, allylcyclohexyl propionate, limonene   |
| Cinnamon              | Estragole, eugenol, limonene  |

The polymerized food-grade monomer also forms a polymer with regions that have an affinity toward certain vitamins that can be absorbed into the microbeads. This can improve the impregnation of the vitamins into the pores of the polymeric beads. These regions are essentially polymeric chains of food-grade monomer. If the vitamin can dissolve into or has an affinity toward the food-grade monomer, the vitamin will likely have an affinity toward the polymeric chains in these regions.

Example VVitamin C Fortified Candy

A. Preparation of Microbeads Impregnated  
With Vitamin C

Microbeads from Example I part A are immersed in an aqueous solution of 20% ascorbic acid (vitamin C).

The beads are soaked for 24 hours in the absence of light. The beads are filtered from the excess solution and are immediately coated by spray chilling with wax.

B. Preparation of Vitamin C Fortified Fruit Slice Candy

The ingredients in Table VI are combined in the manner described below to produce the captioned candy.

Table VI  
JELLY FRUIT SLICES, LEMON

|                                     |       |
|-------------------------------------|-------|
| Sugar                               | 22 lb |
| Corn Syrup                          | 16 lb |
| Water                               | 12 qt |
| Slow-Setting Citrus Pectin          | 8 oz  |
| Sodium Citrate (dissolved in water) | 2 oz  |
| Citric Acid (dissolved in water)    | 4 oz  |
| Yellow Color                        | 2 tsp |
| Oil of Lemon                        | 4 tsp |
| Vitamin C Microbeads                | 2 lb  |

The water is placed in a large copper pan and heated to the boiling point. The pectin is mixed dry with seven pounds of sugar and added to the boiling water, while stirring constantly. When boiling again, the dissolved sodium citrate and one third of the dissolved citric acid are added, while stirring in one third of the dissolved citric acid are added, while stirring in the balance of the sugar and the corn syrup gradually. The batch is cooked to 108°F and is then removed. The microbeads are then added. Two small portions, about five pounds each are taken from the batch and poured into small pans; the largest portion

is kept in the cooking pan. The first small portion is colored yellow, flavored with one teaspoonful of oil of lemon and one teaspoonful of citric acid. This is mixed through well, poured out rapidly on a paper-lined slab, and spread out rapidly to about 1/16 inch thickness.

The second small portion is flavored with one teaspoonful of oil of lemon. One teaspoonful of citric acid is also stirred in. This is then poured on top of the first layer, and spread rapidly and evenly to produce a "peel" layer.

The remaining large portion is colored yellow and flavored with 2 teaspoonfuls of oil of lemon. Four teaspoonfuls of citric acid are stirred into the large batch. The batch is then run out through the funnel rapidly into jelly bar molds and allowed to set. The jellies are then removed, and placed on boards lined with wax paper.

The lemon-peel batch on the slab is turned upside down on the slab and sprinkled with some starch. The paper on top is dampened and removed, and sugar is sprinkled on top. After the lemon-peel batch is turned over again, the lemon jelly bars are wrapped around with the peel, leaving the bottom as it is. The wrapped rolls are rolled in fine granulated sugar and allowed to set until the "peels" adhere to the bars. The jelly is then sliced into fine thin slices and rolled in sugar. After drying, the slices are placed in crystal pans and crystallized in a conventional manner.

#### Example VI

##### Polymeric Beads Including Styrene-Butadiene Rubber

Styrene-butadiene rubber (10.0 g) is dissolved in toluene (90.0 g). In a separate beaker, polyvinylalcohol (1.5 g) is dissolved in water (450.0 g) at about 40°C. The copolymer solution is

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mixed with styrene monomer (150.0 g) and divinylbenzene monomer (30.0 g). Benzoyl peroxide (1.5 g) is added to the mixture, and the mixture is agitated at room temperature. The mixture with copolymer is added to the polyvinylalcohol solution, and the combined mixture is agitated with a motor-driven propeller.

The mixture is heated to 80 - 90°C for at least four hours during which time it is agitated. The mixture is cooled, and filtered to remove the beads. The beads can be used in any of the formulations in the previous examples to produce a vitamin-fortified food.

While several embodiments of the invention have been described, other embodiments will be apparent to those of ordinary skill in the art. Such embodiments are to be included within the scope of the present invention unless the following claims expressly state otherwise.

## WHAT IS CLAIMED IS:

1. A food product, comprising  
a food matrix containing water-insoluble  
porous polymeric beads impregnated with a vitamin.
2. The food product of claim 1 wherein said  
porous polymeric beads are coated with a water-soluble  
coating.
3. The food product of claim 1 wherein said  
porous polymeric beads are coated with a  
water-insoluble coating.
4. The food product of claim 1 wherein said  
vitamin is fat-soluble.
5. The food product of claim 4 wherein said  
vitamin is selected from the group consisting of  
vitamin A, vitamin D or vitamin K, or combinations  
thereof.
6. The food product of claim 1 wherein said  
vitamin is water-soluble.
7. The food product of claim 6 wherein said  
vitamin is selected from the group consisting of  
vitamin B complex or vitamin C, or combinations  
thereof.
8. The food product of claim 1 wherein said  
porous polymeric beads are polymerized from styrene and  
divinylbenzene.

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9. The food product of claim 1 wherein said porous polymeric beads are polymerized from divinylbenzene and a food-grade monomer that can polymerize with divinylbenzene.

10. A method of making a food product, comprising impregnating water-soluble porous polymeric beads with a vitamin; and adding said beads to a food product.

11. The method of claim 10 wherein said food product is a cereal, and said beads are coated on said cereal.

12. The method of claim 10 wherein said food product is a cooked cereal, and said beads are added before cooking.

13. The method of claim 10 wherein said food product is a cereal, and said method further comprises providing said cereal in a wet state, adding said beads to said cereal in said wet state, and drying said cereal.

14. The method of claim 13 wherein said wet cereal is at a temperature below 100°C when said beads are added.

15. The method of claim 10 wherein said beads are coated with a water-soluble coating prior to addition to said food product.

16. The method of claim 10 wherein said beads are coated with a water-soluble coating prior to addition to said food product.

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17. The method of claim 16 wherein said food product is provided in a wet state prior to bead addition, and is dried after bead addition.

18. The method of claim 17 wherein said food product is dried by exposing it to a reduced pressure at a temperature less than 100°C.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US90/00569

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

 IPC (5) : A23L 1/302  
 U.S. Cl : 426/72

**II. FIELDS SEARCHED**

| Classification System   | Minimum Documentation Searched <sup>7</sup> | Classification Symbols |
|---|---|------------------------|
|   |   |                        |
| U.S.  | 426/72,73,302,303,311,520,618               |                        |
| <b>Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></b> |   |                        |

**III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>**

| Category <sup>10</sup> | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup> |  |                   | Relevant to Claim No. <sup>13</sup> |
|------------------------|--|--|-------------------|-------------------------------------|
| Y                      | US,A 4,690,825 (WON)<br>See Entire Document.   |  | 01 September 1987 | 1-18                                |
| Y                      | US,A 3,767,825 (HAMMES)<br>See Entire Document.  |  | 23 October 1974   | 1-18                                |
| A                      | US,A 4,675,236 (OHKAWARA)  |  | 23 June 1987      | 1-18                                |
| A                      | US,A 4,230,687 (SAIR)  |  | 28 October 1980   | 1-18                                |
| A                      | US,A 4,102,806 (KONDO)   |  | 25 July 1978      | 1-18                                |
| A                      | US,A 4,038,422 (KEYSER)  |  | 26 July 1977      | 1-18                                |
| A                      | US,A 3,782,963 (DUVALL)  |  | 01 January 1974   | 1-18                                |
| A                      | US,A 3,767,824 (KEYSER)  |  | 23 October 1973   | 1-18                                |

 \* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

27 April 1990

Date of Mailing of this International Search Report

21 MAY 1990

Signature of Authorized Officer

R. B. Penland

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